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<p>(21) International Application Number: PCT/GB93/01419</p> <p>(22) International Filing Date: 6 July 1993 (06.07.93)</p> <p>(30) Priority data: 9214765.1 11 July 1992 (11.07.92) GB</p> <p>(71) Applicant (<i>for all designated States except US</i>): SMITH-KLINE BEECHAM PLC [GB/GB]; New Horizons Court, Brentford, Middlesex TW8 9EP (GB).</p> <p>(72) Inventor; and (75) Inventor/Applicant (<i>for US only</i>): PAGE, David, John [GB/GB]; SmithKline Beecham Consumer Brands, St. George's Avenue, Weybridge, Surrey KT13 0DE (GB).</p>		<p>(74) Agent: WALKER, Ralph, Francis; SmithKline Beecham, Corporate Patents, Great Burgh, Yew Tree Bottom Road, Epsom, Surrey KT18 5XQ (GB).</p> <p>(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report.</i></p>	
<p>(54) Title: PRESSURISED AEROSOL FORMULATION</p> <p>(57) Abstract</p> <p>A pressurised aerosol formulation in a pressurised container which is in the form of a compressed gas, a liquefied hydrocarbon propellant and also active compound(s) and carrier(s) which are in the form of a suspension or a solution and which contains at least 0.05 per cent by weight of compressed gas and at least 0.5 per cent by weight of liquefied hydrocarbon propellant.</p>			

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PRESSURISED AEROSOL FORMULATION

- The present invention relates to propellants used in pressurised spray containers particularly those of the type known as aerosol cans.
- Traditionally these systems use liquefied propellants, which have the ability to change from the gaseous to liquid state (below the critical temperature) when pressure is applied. Examples of liquefied propellants are hydrocarbon and chlorofluorocarbons.
- 10 The liquefied propellant is contained in the packaging and it divides between the liquid and gaseous phases, with the liquid phase forming a reserve. On spraying the container, part of the gaseous phase is expelled. Immediately a part of the liquid phase vaporises, returning the internal pressure almost to its original starting pressure. The pressure remains substantially constant throughout the life of the container.
- 15 The pressurised containers are equipped with a dispensing head and valve and pressurised with the liquefied propellant. Upon discharge of the concentrate through the dispensing head the volatilisation of the dispensed liquid propellant particles assists the dispensed product to form aerosol droplets. This change from the liquid to gaseous phase may also have a self cleaning action to remove any residual
- 20 concentrate which may have remained within the expansion chamber and channels of the dispensing head after spraying has ceased.
- A disadvantage of hydrocarbon propellants is that they are by nature flammable and the possibility of an explosion exists if the hydrocarbon/air ratio is between the upper and lower explosive limits. Products using hydrocarbon
- 25 propellants therefore require careful handling, storage and transportation. Also, for environmental reasons, the future use of hydrocarbon propellants may be restricted.
- One alternative to using liquefied gases is to use compressed gas as the propellant system. Various compressed gas containing products have been successfully marketed using carbon dioxide. However, the use of carbon dioxide
- 30 may also in the future be restricted for environmental reasons. Nitrogen is suitable for use as a compressed gas propellant, it is non toxic, non-flammable and environmentally friendly. There are, however, some disadvantages to using nitrogen as an aerosol propellant. Because the nitrogen is only present as a gas, there is no liquid state present (unlike the liquefied propellants) to form a pressure reserve.
- 35 Typically only 1 - 2 g of nitrogen can be filled into an aerosol package. Any misuse of the aerosol package resulting in loss of the nitrogen propellant may prevent total evacuation of the contents.

Nitrogen propellant systems rely on the use of mechanical means involving the use of small diameter channels in the dispensing head to create the aerosol particles. This is because there is no liquid to gas transformation as with the liquefied propellants. Nitrogen does not have the self cleaning action of the liquefied

- 5 propellants and therefore any product remaining in the channels after spraying will quickly lead to impaired performance and may even result in total blockage.

The nitrogen is added to the aerosol container by filling to a typical pressure of 120 psig. As the contents are dispensed there is a pressure drop within the can to around 30 - 40 psig after total evacuation of the contents. This pressure drop may

- 10 affect the break up characteristics of the valve with a gradual transition from fine to coarse aerosol particles as the pressure decreases.

The use of nitrogen as the sole aerosol propellant also results in performance differences compared to a liquefied propellant system e.g. hairspray formulation gives a significantly wetter spray, taking longer to dry, forming globules of product

- 15 on the hair and generally giving an inferior performance.

For these reasons we have found it desirable to provide a mixture of compressed gas and liquefied propellant which are to be sprayed from a pressurised gas container as a cosmetic, household or medicinal spray of propellant gases to:-

- 20 1) Provide a small reservoir of liquefied propellant to ensure total evacuation of the contents in the case of misuse.

2) Provide the self cleaning action of liquefied propellants to prevent blockage of the dispensing head.

3) Ensure constant spray characteristics throughout the life of the can.

- 4) Improve the product's performance to give parity with that of a typical liquefied propellant system.

25 5) Reduce the flammability of the product in comparison to a liquefied propellant system.

The present invention therefore provides a pressurised aerosol formulation in a pressurised container which is in the form of a compressed gas, a liquefied

- 30 hydrocarbon propellant and also active compound(s) and carrier(s) which are in the form of a suspension or a solution and which contains at least 0.05 per cent by weight of compressed gas and at least 0.5 per cent by weight of liquefied hydrocarbon propellant.

Suitable compressed gases are nitrogen, carbon dioxide, compressed air,

- 35 oxygen, xenon, argon or mixtures thereof.

Suitable liquefied hydrocarbon propellants are methane, ethane, butane, propane, isobutane, dimethyl ether, pentane, hexane, heptane, octane, nonane,

decane, chlorodifluoromethane, 1,1 dichloro, 2,2,2 trifluoroethane, 1,2 dichloro, 2,2, difluoroethane, 2 chloro, 2,2 difluoroethane, 1,2,2,2 tetrafluoroethane, 2,2,2 trifluoroethane, 1,1,1 trichloroethane, dichloromethane, or mixtures thereof.

Suitable carriers are volatile compounds, for example alcohols, and include

- 5 ethyl alcohol, n-propanol, iso-propanol, n-pentane, iso-pentane, water, acetone, ethyl, methyl ketone, diethyl ether, volatile silicone compounds, fluoro surfactants, dimethoxy methane, diethyl carbonate, methoxy acetone, hydroxy acetone, methyl isopropyl ketone, diethyl ketone, diisopropyl ketone, dipropyl ketone, diacetone alcohol, or mixtures thereof.
- 10 The formulation according to this invention can be formulated with cosmetic, hygienically or medicinally active constituents (active compounds) and give formulations for different purposes eg. cosmetic spray.

- 15 Active compounds which can be contained in the formulation are eg. hair spray resin, hair care substances, deodorants, antiperspirants, perfume, bactericidal agents and fungicides.

Examples of such actives being 2,4,4' trichloro-2'-hydroxydiphenylether which is sold by Ciba Geigy and is known internationally under the non-proprietary name of Triclosan, and octylamide/ acrylate/ butylaminoethyl methacrylate, a hairspray resin which is sold by National Starch Ltd. and is sold under the name Amphomer LV71.

- 20 It may also be necessary to include in certain formulations other ingredients such are conventional in the art, for example neutralisers for hairspray resins such as amino-methylpropanol, otherwise known as AMP.

- 25 A typical aerosol formulation preferably contains as propellant gases 0.05 to 2.5 per cent by weight of nitrogen and 1.0 to 12.0 per cent by weight of liquified hydrocarbon, the percentages by weight being based on the total weight of the constituents of the filled container.

- 30 The aerosol formulation preferably contains 80 - 95 per cent by weight of a carrier, suitably an organic carrier for the propellant gases and/or active compound(s), the percentages by weight being based on the total weight of the constituents of the filled container.

- 35 Ideally the aerosol formulation is characterised in that it contains 0.7 - 1.4 per cent by weight of nitrogen, 4 - 9 per cent by weight of liquified hydrocarbon, 85 - 93 per cent by weight of an organic carrier, suitably alcohol, and 1 to 4 per cent of active compound by weight.

- 35 The nature and the amount of the required active compound, organic solvent for the propellant gases and/or active compound, and nitrogen are so matched qualitatively and quantitatively in a sample batch taking into account the intended use

and taking into account the ranges given above for the percentages by weight that a suspension or solution is obtained which can be sprayed without blocking nozzles or channels as a ready to use aerosol.

- The present invention also provides a process for the manufacture of an aerosol formulation which is characterised in that the active compound(s), and carrier(s) are processed such that a requisite partial amount is filled into a pressurised spray container and subsequently sealed with a valve. After the liquefied hydrocarbon propellant and nitrogen have been filled through the valve into the container under pressure, the liquid product is in the form of a suspension or homogeneous solution under a pressure of about 120 psig.

The invention is illustrated by the following Examples wherein all figures refer to % w/w.

EXAMPLES**Hairsprays**

	1	2	3	4
Hairspray Resin	0.57	1.13	1.9	2.27
AMP	0.098	0.196	0.294	0.392
Silicone	0.05	0.10	0.15	0.20
Alcohol	95.952	92.244	87.526	86.808
Perfume	0.17	0.17	0.17	0.17
Nitrogen	1.16	1.16	1.16	1.16
Hydrocarbon	2.00	5.00	9.00	9.00

5

Deodorant Sprays

	5	6
Triclosan	0.10	0.10
Alcohol	95.74	95.74
Perfume	1.00	1.00
Nitrogen	1.16	1.16
Hydrocarbon	2.00	-
Dimethyl Ether	-	2.00

Claims

1. A pressurised aerosol formulation in a pressurised container which is in the form of a compressed gas, a liquefied hydrocarbon propellant and also active compound(s) and carrier(s) which are in the form of a suspension or a solution and which contains at least 0.05 per cent by weight of compressed gas and at least 0.5 per cent by weight of liquefied hydrocarbon propellant.
- 5 2. An aerosol formulation according to claim 1, wherein the compressed gas is nitrogen, carbon dioxide, compressed air, oxygen, xenon, argon or mixtures thereof.
- 10 3. An aerosol formulation according to claim 2, wherein the liquefied hydrocarbon propellant is methane, ethane, butane, propane, isobutane, dimethyl ether, pentane, hexane, heptane, octane, nonane, decane, chlorodifluoromethane, 1,1 dichloro, 2,2,2 trifluoroethane, 1,2 dichloro, 2,2, difluoroethane, 2 chloro, 2,2 difluoroethane, 1,2,2,2 tetrafluoroethane, 2,2,2 trifluoroethane, 1,1,1 trichloroethane, dichloromethane, or mixtures thereof.
- 15 4. An aerosol formulation according to claim 3, comprising 80-95 per cent by weight of carrier(s), the carrier(s) being volatile compound(s).
- 20 5. An aerosol formulation according to claim 4, wherein the carrier(s) are ethyl alcohol, n-propanol, iso-propanol, n-pentane, iso-pentane, water, acetone, ethyl, methyl ketone, diethyl ether, volatile silicone compounds, fluoro surfactants, dimethoxy methane, diethyl carbonate, methoxy acetone, hydroxy acetone, methyl isopropyl ketone, diethyl ketone, diisopropyl ketone, dipropyl ketone, diacetone alcohol, or mixtures thereof.
- 25 6. An aerosol formulation according to any one of claims 1 to 5 comprising 0.05 to 2.5 per cent by weight of nitrogen and 1.0 to 12.0 per cent by weight of liquefied hydrocarbon.
- 30 7. An aerosol formulation according to claim 6 comprising as active compound(s), hair spray resin, hair care substances, deodorants, antiperspirants, perfume, bactericidal agents or fungicides.
- 35 8. An aerosol formulation according to claim 7 comprising 2,4,4'trichloro-2'-hydroxydiphenylether.

9. A process for the manufacture of an aerosol formulation which is characterised in that the active compound, and carrier(s) are processed such that a requisite partial amount is filled into a pressurised spray container, sealed with a valve and thereafter the liquified hydrocarbon propellant and compressed gas introduced into the liquid product.
- 5
10. A process according to claim 11, wherein the liquid product is in the form of a suspension or homogeneous solution under a pressure of about 120 psig.
- 10 11. An aerosol formulation according to any one of claims 1 to 8, for use with cosmetic, hygienically or medicinally active constituents.
12. An aerosol formulation according to claim 11 for use as a cosmetic, household or medicinal spray.

15

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 93/01419

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C09K3/30; A61K7/00; A61K9/12

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
Int.Cl. 5	C09K ; A61K

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are included in the Fields Searched⁸III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	DATABASE WPI Week 8517, Derwent Publications Ltd., London, GB; AN 85-102733 & JP,A,60 048 915 (KOIKE KAGAKU) 16 March 1985 see abstract --- PATENT ABSTRACTS OF JAPAN vol. 006, no. 085 22 May 1982 & JP,A,57 018 776 (NAKAMURA TAKASHIGE) 30 January 1982 see abstract ---	1,4,5,7
X	---	1,2,3,7, 11 -/-

⁶ Special categories of cited documents :¹⁰

- "A" document defining the general state of the art which is not considered to be of particular relevance
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⁷ "T" late document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention⁸ "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step⁹ "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art¹⁰ "A" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

02 SEPTEMBER 1993

Date of Mailing of this International Search Report

16.09.93

International Searching Authority

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Signature of Authorized Officer

NICOLAS H.J.F.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category ^a	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
P,X	<p>DATABASE WPI Week 9246, Derwent Publications Ltd., London, GB; AN 92-375607 & JP,A,4 273 807 (MANDOM) 30 September 1992 see abstract</p> <p>---</p>	1,2,3,7
X	<p>US,A,3 387 425 (FLANNER) 11 June 1968 see claims 1-5 see column 3, line 14 - line 18</p> <p>---</p>	1-3,7-11
X	<p>PATENT ABSTRACTS OF JAPAN vol. 011, no. 133 25 April 1987 & JP,A,61 271 212 (TOYO AEROSOL) 1 December 1986 see abstract</p> <p>---</p>	1-3,7
X	<p>FR,A,2 217 405 (JOHNSON & SON) 6 September 1974 see claims 1-6 see page 4, line 3 - page 5, line 8</p> <p>-----</p>	1-3,7,11

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9301419
SA 76807

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-3387425		None		
FR-A-2217405	06-09-74	US-A-	3970584	20-07-76
		AU-A-	6441574	10-07-75
		CA-A-	1027868	14-03-78
		DE-A,C	2406109	22-08-74
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		NL-A-	7401544	16-08-74